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Polystyrene–Poly(sodium methacrylate) Amphiphilic Block Copolymers by ATRP: Effect of Structure, pH, and Ionic Strength on Rheology of Aqueous Solutions

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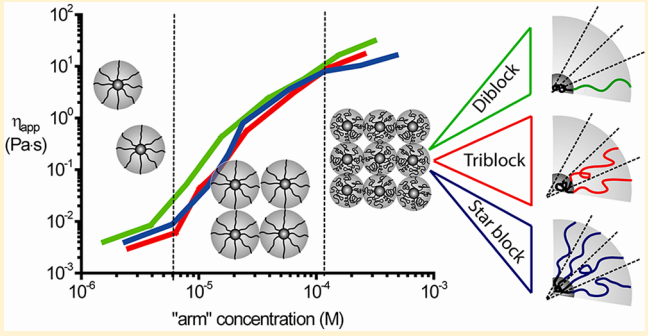
Supporting Information

ABSTRACT: Three well-defined polystyrene–poly(sodium methacrylate) amphiphilic block copolymers characterized by different molecular architecture (diblock, triblock, and four-arm star) have been synthesized by ATRP. The rheology of their water solutions has been evaluated by measuring dynamic moduli and shear viscosity at different concentrations. All polymers show remarkable thickening properties and a sol–gel transition at low concentration (0.1 wt %). Above the gel concentration the solutions are shear thinning without an apparent Newtonian plateau. The observed viscosity profile can be interpreted in terms of percolation theory applied to highly stretched polymeric micelles, which start to contract above the percolation threshold. An interesting correlation between solution viscosity and concentration of hydrophilic block (defined here as "arm concentration") has been observed, giving indirect evidence for the arrangement of the polymers into micelles. The influence of ionic strength and pH on the rheology of these systems has also been preliminary investigated.



INTRODUCTION

Amphiphilic block copolymers have been receiving great interest over the past decades for their ability to self-assemble in stable micelles or other aggregates in a selective solvent, in most cases water. When the water solubility of at least one block is dependent on external parameters such as temperature or pH, they can also exhibit stimuli-responsive behavior. Their characteristics allow controlling interfacial properties and fluid rheology and thus provide good candidates for applications in diverse areas ranging from latex stabilization and coatings to biomedical engineering and enhanced oil recovery.[1−10] For example, in the case of enhanced oil recovery (EOR), it is known that mobilization of residual oil from a reservoir by injection of a water solution is mainly influenced by the viscosity of the displacing phase and the interfacial tension between the water phase and the oil.[11,12] Thickening agents such as water-soluble high molecular weight polymers,[13] in combination with surfactants,[11] are often used in EOR for this reason. The possibility of using amphiphilic copolymers for applications in EOR is therefore interesting, as an effect on both rheology and interfacial properties of water may be expected.

Despite the large number of publications concerning synthesis and self-assembly of amphiphilic block copolymers, a systematic study of the rheology of these systems is still missing. This is somewhat surprising, considering its importance for most of the applications.

The most studied polymers are AB diblock and ABA or ABC triblock (telechelic) copolymer in which the hydrophilic block B is constituted by poly(ethylene oxide) (PEO) or poly(acrylic acid) (PAA) and the hydrophobic blocks by polystyrene or aliphatic alkyl chains.[14−16] Polymers containing different hydrophobic[17] or hydrophilic[18] blocks have also been subject of rheological studies. All these polymers form viscoelastic solutions which turn to gels at a certain critical concentration, depending on the composition and the architecture of the polymer. Polymers containing a polyelectrolyte chain such as PAA are of particular interest because the presence of Columbic forces and osmotic effects lead to highly stretched conformations in solution. This causes micelles to overlap at relatively low concentrations and delivers interesting rheological properties (gelation, non-Newtonian behavior, sharp changes in viscosity). Moreover, the charge density and the extent of ionic interactions are dependent on pH and ionic strength, and consequently the rheology can be tuned by acting on these parameters.[19] Also, the addition of surfactants can

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have an influence on the rheological behavior of block polyelectrolytes.[17]

Rheology of diblock PS-*b*-PAA in water has been investigated.[14,15,20,21] In water solutions, their aggregates are normally constituted by a dense rigid PS core surrounded by a hydrophilic corona of PAA brushes. The rheological properties of these polymeric micelles are determined by the interactions between the coronas, but little is known about the mechanism.[20] Regardless of the mechanism, at sufficiently high concentrations the micelles are forced into a densely packed structure. A sol−gel transition is observed above a percolation threshold.[21] For PS−PAA and related block copolymers, the gel structure can be described as a disordered state, similar to a colloidal glass.[21,22]

The molecular architecture of the polymers largely affects their self-assembly, which in turn regulates the rheology. A very detailed rheological study of telechelic ABA and ABC copolymers with a charged PAA or PMAA hydrophilic middle block has been performed by Tsitsilianis and co-workers.[23−27] Their aggregation behavior and rheology have been found to be different from those of the corresponding PS-*b*-PAA diblock copolymers. In this case, depending on the concentration and the compatibility of the hydrophobic blocks, the two associative blocks assemble either into the same core, forming "flower-like" micelles, or into different cores, forming bridges and thus a gel via formation of transient networks. Recently, the same mechanism of formation of intermolecular connections via the hydrophobic extremities has been proposed to interpret the rheological behavior of four arm star-block copolymers with a hydrophilic PAA core and PS arm ends.[28,29]

The rheology of analogous PS-*b*-PMAA diblock copolymers is basically unexplored. The presence of an extra methyl group on the monomer increases the hydrophobicity of PMAA with respect to PAA with a subsequent influence on polymer aggregation behavior in water.[4,30,31] Consequently, a different rheological behavior can be expected. For example, it has been shown that if hydrophobic groups are present in the polyelectrolyte block, these can act as "stickers", favoring the gelation of the system. PS-*b*-(AA-*co*-EA) copolymers show a decrease in the gelation concentration and an increase in viscosity by increasing the number of EA groups scattered along the AA block.[14] Also, to the best of our knowledge, the rheology of triblock or star PS−PAA or PS−PMAA copolymers with a central hydrophobic block and hydrophilic arms has not yet been investigated.

Radical controlled polymerization methods (ATRP, NMP, RAFT) allow the synthesis of well-defined amphiphilic copolymers characterized by different molecular weight and structure (di-, tri-, and multiblock, comb, star).[32−36] This has provided a boost in the study of structure−property relationships of PAA (and many others) amphiphilic copolymers. These synthetic tools allow systematic investigations on the influence of molecular architecture on the chemical and physical properties of amphiphilic block copolymers.

In order to determine the most relevant structural features for specific applications, attention should be paid to study the effect of molecular architecture of amphiphilic block polyelectrolytes on their rheology. In this work we present an investigation concerning the rheological behavior of a series of amphiphilic PS−PMAA copolymers with different architectures (diblock, triblock, and four-arm star). The influence of hydrophobic and hydrophilic block length of diblock PS−PMAA is also of interest and is the subject of a forthcoming publication.[37] The polymers have been prepared by ATRP of styrene on a monofunctional, difunctional, and tetrafunctional initiator, respectively, followed by ATRP of tBMA and subsequent hydrolysis, as reported in the literature.[38] The rheological features of water solutions at different polymer concentrations have been explored and compared. The behavior of the triblock systems at different pH and concentration of NaCl has also been investigated.

EXPERIMENTAL SECTION

Styrene (Sigma-Aldrich, ≥99%) and *tert*-butyl methacrylate (tBMA, Aldrich, 98%) were vacuum-distilled over CaH_2 and kept under nitrogen before use. Glacial acetic acid, ethanol, ethyl acetate, THF, dioxane, methanol, and acetone were used without further purifications. CuCl (Sigma-Aldrich, ≥99%) and CuBr (Sigma-Aldrich, ≥98%) were stirred in glacial acetic acid for at least 5 h and then filtered, washed with acetic acid, ethanol, and ethyl acetate, and dried under vacuum before use. Anisole (Sigma-Aldrich, anhydrous, 99.7%) was deoxygenated by bubbling with nitrogen for at least 30 min before use. 1-Methyl-2-bromopropionate (MBP, Aldrich, 98%), ethylene bis(2-bromoisobutyrate) (EBIB, Aldrich, 97%), pentaerytritoltetrakis-(2-bromoisobutyrate) (PETBIB, Aldrich, 97%), tetramethylethylenediamine (TMEDA, Aldrich, ≥99.5%), and tris[2-(dimethylamino)ethyl]-amine (Me_6TREN, Aldrich) were used as received, without further purifications.

Synthesis of Polystyrene Macroinitiator (PS-Br). PS-Br macroinitiators were synthesized as follows: 1 mmol of initiator (MBP, EBIB, or PETBIB), CuBr (1−4 mmol), and styrene (120−200 mmol, 11.35−19.00 mL) were introduced under nitrogen in a 100 mL round-bottomed flask equipped with a magnetic stirring bar and a reflux condenser, previously purged with nitrogen . The apparatus was put in an oil bath set to a temperature of 100 °C. After 1 min, TMEDA (1−4 mmol) was introduced under nitrogen. After a given time, the reaction was stopped by cooling down, introducing air, and diluting with around 50 mL of THF. The THF solution was filtered through a short column of alumina (about 5 cm) to remove the copper catalyst and then precipitated in a 20-fold excess of methanol. The precipitate was filtered, redissolved in THF, and reprecipitated in 2:1 v/v methanol/water, washed with methanol, and dried overnight at 60 °C, affording a white solid. The conversion and the molecular weight were determined both gravimetrically and by GPC.

Synthesis of Block Copolymers PS−PtBMA. PS-Br macroinitiator (1 g), deoxygenated anisole (10 mL), the copper catalyst, and tBMA (according to stoichiometry) were introduced under nitrogen in a 250 mL round-bottomed flask equipped with magnetic stirring bar and reflux condenser, previously purged with nitrogen. After complete dissolution of the macroinitiator, the flask was put in an oil bath at 90 °C and the ligand (Me_6TREN) was added under nitrogen. After a given time, the reaction was stopped by cooling down, introducing air, and diluting with around 50 mL of THF. The THF solution was filtered through a short column of alumina to remove the copper catalyst, then precipitated in a 20-fold excess of methanol, redissolved in THF and reprecipitated in 2:1 methanol/water mixture twice, washed with methanol, and dried overnight at 60 °C, affording a white solid. The conversion and the molecular weight were determined both gravimetrically and by NMR.

GPC Measurements. GPC measurements were performed with a HP1100 from Hewlett-Packard, equipped with three 300 × 7.5 mm PLgel 3 μm MIXED-E columns in series. Detection was made with a GBC LC 1240 IR detector. The samples were prepared by dissolving the isolated polymers in THF at 10 mg/mL concentrations and using toluene as internal standard. The samples were eluted with THF at a flow rate of 1 mL/min, at a pressure of 140 bar. Molecular weights and PDI were determined using the software PSS WinGPC Unity from Polymer Standard Service. Polystyrene standards were used for calibration.

Hydrolysis and Neutralization. About 3 g of PS−PtBMA precursor was dissolved in 100 mL of dioxane in a 250 mL round-bottomed flask equipped with magnetic stirring bar and reflux

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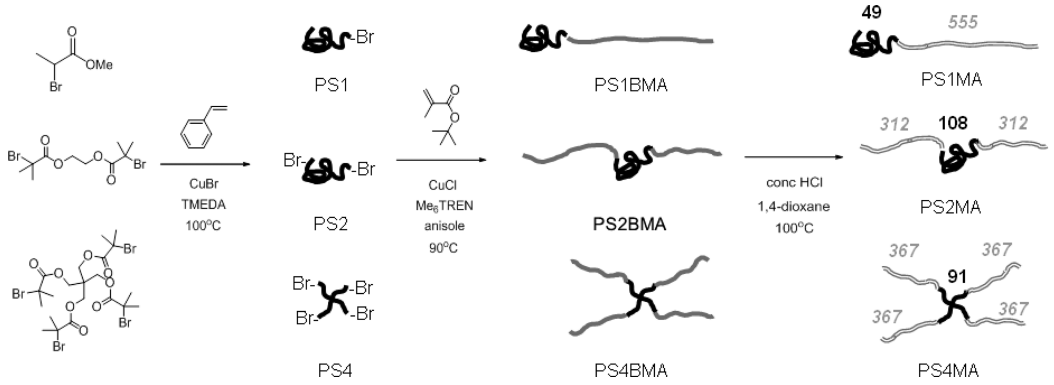
Scheme 1. Synthesis and Structures of the Polymers Prepared in This Work[a]



[a]The numbers indicate the polymer composition (see also Supporting Information).

condenser at 100 °C (at low temperature the dissolution is quite slow). After complete dissolution, an excess of concentrated HCl (10 mL) was added. The solution turns from transparent to cloudy in about 1 h. After 3 h the reaction was stopped by cooling (the solution turns back to transparent). The solid was recovered by precipitating the mixture in an excess of acetone and then drying at 60 °C overnight. The polymers were recovered as glassy transparent whitish solids, depending on the isolation procedure. The extent of hydrolysis was determined by NMR in d_6-DMSO.

The corresponding sodium salts were obtained by dissolving the polymers in an excess of NaOH in water, then removing the excess base by dialyzing against Milli-Q water, changing water at least 3 times over a period of 2 days, and then drying at 60 °C for 3 days. The products were recovered as glassy transparent white-yellowish solids.

pH Potentiometric Measurements. Potentiometric measurements were performed with a Metrohm 691 pH meter, calibrated with buffers at pH 4.01 and 6.98.

Rheology Measurements. Solutions at 0.5, 1.0, and 2.0 wt % concentrations were prepared by dissolving the sodium salts in Milli-Q water, followed by stirring for at least 10 h before the measurement in order to get homogeneous solutions. Solutions at lower concentrations were prepared by dilution of aliquots of the concentrated solutions. All the prepared polymers were soluble in water in their sodium salt form, without the need for cosolvents or heating. The solutions are in general stable for months (no appearance of precipitate or phase separation, reproducible measurements). The measurements were performed with a Haake Mars III rotational rheometer at 20 °C, using 2 mL of solution. A trap for the solvent was used in order to avoid water evaporation during the measurements. An amplitude sweep experiment was performed for every solution in order to establish the regime of viscoelastic response. Oscillation frequency sweeps were performed at constant stress.

RESULTS AND DISCUSSION

Synthesis. The syntheses of mono-, di-, and tetrafunctional PS-Br macroinitiators were performed in bulk at 100 °C, using CuBr as catalyst and TMEDA as ligand. Chain extension with tBMA was performed in anisole at 90 °C, using CuCl or CuBr as catalyst and Me_6TREN as ligand. Hydrolysis has been conducted with concentrated HCl in refluxing dioxane, according to a standard procedure. Primary ester groups, present in the di- and tetrafunctional initiator, are stable in the adopted hydrolysis conditions.[39,40]

The synthesis and the structure of the obtained polymers are sketched in Scheme 1. Details on synthesis and characterization are available as Supporting Information.

The polymers do not dissolve in water in the acidic form but swell very slowly. Upon addition of NaOH, complete solubility is achieved and the viscosity of all solutions increases dramatically. The polymers in the fully neutralized form are obtained by adding an excess of base and then dialyzing the resulting solution against Milli-Q water. In the salt form all the polymers are readily soluble in water, forming clear colorless or slightly cloudy (at higher concentrations) solutions. Because of the high viscosity, the solutions were stirred for at least 10 h to ensure homogeneity.

Rheology. The polymers possess remarkable thickening properties. All the solutions are shear thinning with no apparent Newtonian plateau in the frequency range investigated, except for the very diluted ones (<0.05 wt %). The shear viscosity profiles of 1 wt % solutions of the three polymers are basically superimposable (Figure 1). A fit with a power-law fluid model

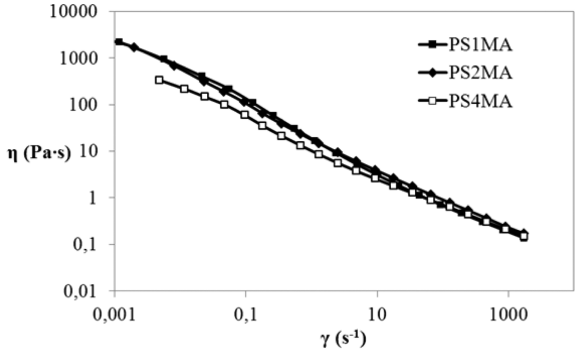


Figure 1. Shear viscosity of 1 wt % solutions.

($\eta = K\gamma^{n-1}$) of the more concentrated solutions (>0.1 wt %), provides a n value of approximately 0.3 for every sample, which is the same as found for PS-*b*-PAA.[14] Attempts to extrapolate the zero-shear viscosity by creep and frequency sweep experiments failed because it was never possible to reach the regime of terminal viscous response. In the first case, no steady-state compliance was reached in reasonable times, while for the second $\lim_{\omega\to 0} G''(\omega)/\omega$ did not reach a constant value at the lowest measurable frequencies. The absence of a Newtonian plateau in the measurable range is typical for amphiphilic block polyelectrolytes gels.[14]

At concentrations in the range 0.5−1 wt %, the solutions form viscoelastic gels, with $G' > G''$ over a broad frequency range (Figure 2) and moduli nearly independent or slightly dependent from ω, as typically observed for viscoelastic gels with a yield stress.[14] Indeed, at 1 wt % the gels do not flow in tube inversion tests. At lower concentrations, the G' and G''

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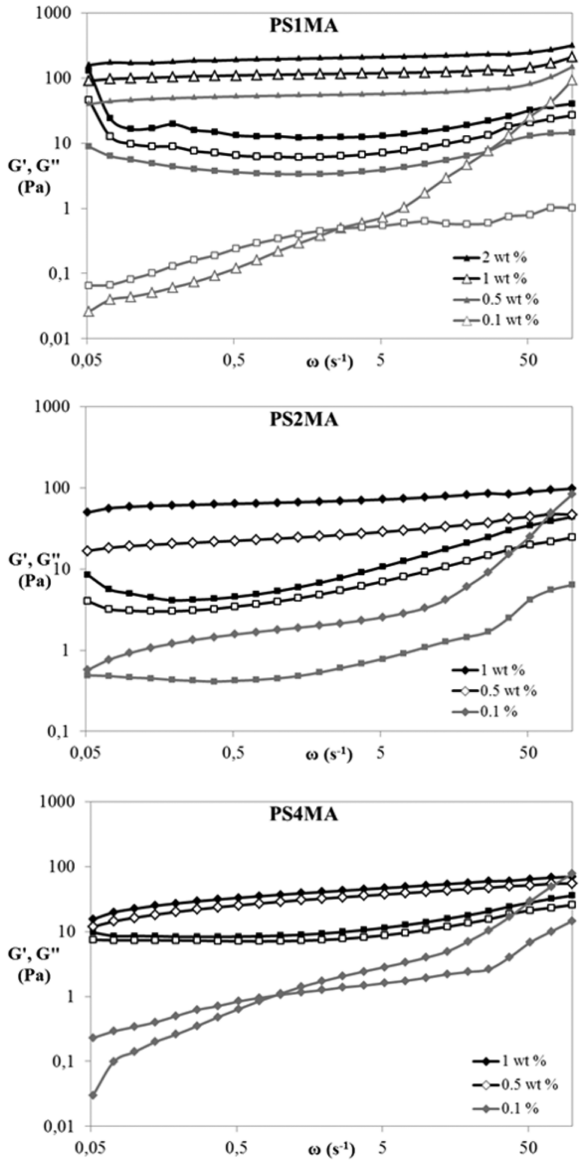

Figure 2. Storage (diamonds) and loss (squares) moduli of solutions at different concentrations.

start to cross and their dependence from ω become more pronounced, indicating the transition from elastic gels to viscoelastic solutions.[21]

In Figure 3, the apparent viscosity ($\dot{\gamma} = 1\ s^{-1}$) as a function of the molar concentration is reported. In all cases a sigmoidal curve is obtained. This trend resembles the one observed for PS−PAA−PnBA terpolymers.[26] The first part of the curve can be interpreted in terms of scaling concepts valid for solutions of linear polymers,[41] later verified also for star polymers and micelles.[42,43] According to the theory, the viscosity starts to increase sharply at the overlapping concentration c^*. Above c^*, in the semidiluted regime, the micelles start to interpenetrate and shrink, with subsequent increase of volume fraction until the percolation threshold for gelation is reached. This suggests that in the terminal region the volume fraction is approaching its geometrical maximum, and there is only further shrinking of the corona (Figure 3). As pointed out by a reviewer, the schematic structure of the gel presented in Figure 3 could be misleading because it appears to be arranged in an ordered state. Actually, most of the evidence of the gel structure in

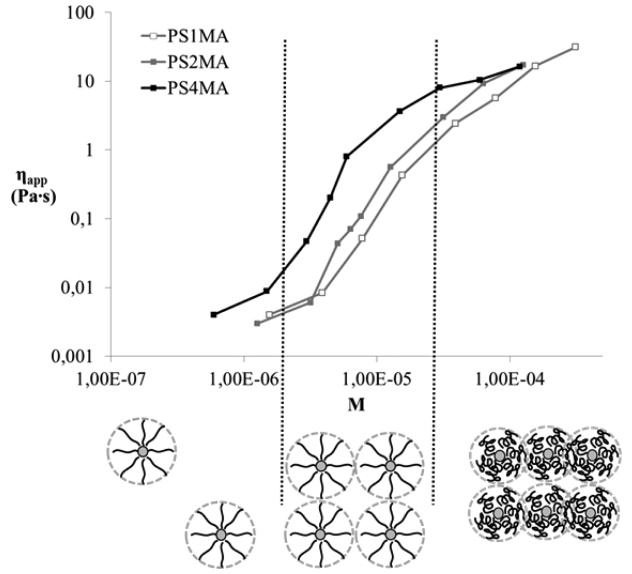

Figure 3. Apparent viscosity (at shear rate = 1 s^{-1}) as a function of concentration and schematic representation of micelles overlapping and shrinking in the different regions.

copolymers similar to the ones presented in this work suggests that the gel structure is a disordered state, analogous to a colloidal glass.[21,22] On the other hand, the gels formed by Pluronic-type copolymers and related systems (e.g., PEO−PPO−PEO, PEO−PBO−PEO, etc.) often do have the micelles in an ordered array. Determination of the gel structure for the present systems would require more structural characterization, which is beyond the scope of this work.[44]

The overlapping concentration follows the order PS4MA < PS2MA ∼ PS1MA. The curves of PS1MA and PS2MA, which have approximately the same monomer composition, are practically superimposable. Interestingly, if the viscosity is plotted against the "arm concentration" (c for PS1MA, $2c$ for PS2MA, and $4c$ for PS4MA), the curves become all almost superimposable, with the one of PS1MA being only slightly shifted to the left at low concentrations (Figure 4).

These observations are consistent with a hypothetic structure of the micelles depicted in Figure 5. Within this assumption, the overlapping concentration order observed in Figure 4 can be justified by the different arm length: the polymer with longer hydrophilic block (PS1MA) forms micelles with longer arms

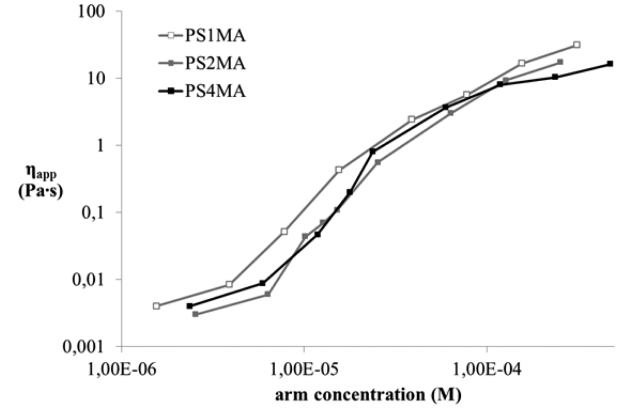

Figure 4. Apparent viscosity (at shear rate = 1 s^{-1}) as a function of "arm concentration".

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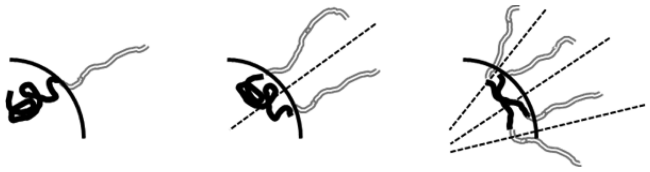

Figure 5. Schematic representation of the arrangement of the polymers into micelles.

and thus starts to overlap at a lower "arm concentration". The PMAA block length is approximately the same for PS2MA and PS4MA, and so is the overlapping "arm concentration". Thus, from a rheological point of view, the triblock and the star block copolymers appear to be equivalent to a diblock copolymer with respectively half and one-fourth the concentration.

pH and Salt Effect. The effect of pH and presence of NaCl on the shear viscosity of 1 wt % PS2MA solutions has been preliminarily investigated. In Figure 6a, the viscosity at shear

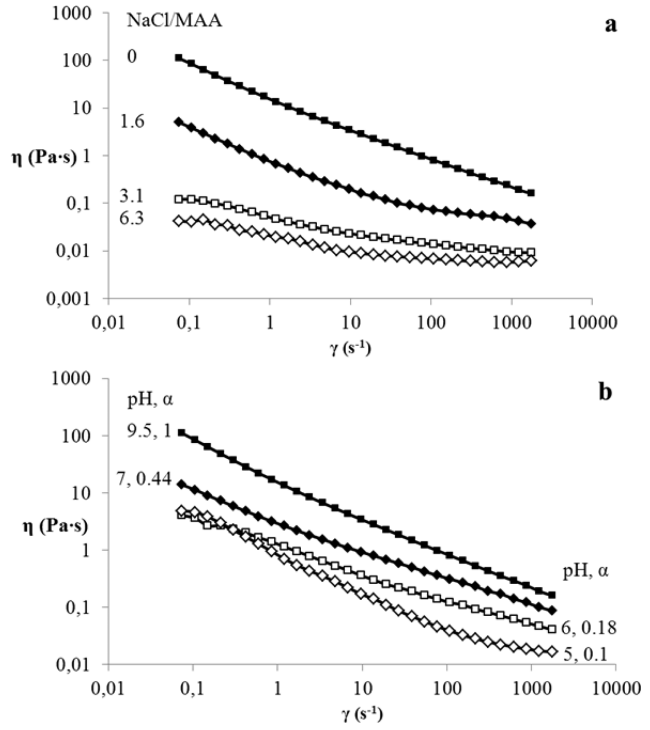

Figure 6. Shear viscosity of PS2MA solutions at different NaCl concentrations (a) and pH (b).

rate = 1 s^{-1} is reported as a function of the NaCl/MAA molar ratio. As expected, upon addition of salt the viscosity dramatically drops, due to corona shrinking. To investigate the effect of pH, PS2MA in the acidic form was suspended in water and powdered NaOH was added in portions. After every addition, a sample was taken for rheological measurements. Potentiometric measurements of pH required at least half hour for equilibration. The solutions show an increase in viscosity with pH and thus with degree of neutralization α (Figure 6b). The viscosity and pH of the fully neutralized solution (α = 1) match those of the same polymer prepared by dialysis.

CONCLUSIONS

In this work, three polystyrene–poly(sodium methacrylate) block copolymers with different molecular architectures were synthesized by ATRP, and the rheology of their water solutions was investigated. Analogously to other amphiphilic block polyelectrolyte of different nature and structure, the polymers form strong viscoelastic gels at relatively low concentration, due to formation of micelles with highly stretched corona. The viscosity versus concentration profiles show at least three different regimes. The transition from the diluted to the semidiluted regime has been interpreted in terms of overlapping concentration, derived from scaling theory for polymers solutions, while the transition from semidiluted to concentrated regime can be rationalized in terms of percolation theory for gelation of hard spheres. The rheological behavior for the triblock and the star copolymers is basically equivalent to that of a diblock copolymer with respectively half and one-fourth the concentration. Preliminary investigations show that—as expected—pH and ionic strength have a great influence on the rheology of the prepared systems.

Despite the fact that the great importance of block polyelectrolytes for many applications is related to their rheology, the literature concerning this subject is still far from exhaustive. In particular, systematic studies about the dependence of rheology on the macromolecular structure are rare. Our focus is on providing more insight into the influence of the molecular architecture of amphiphilic block polyelectrolytes on their rheological behavior. In a forthcoming publication, also the effect of the hydrophobic and hydrophilic block length on the rheology of amphiphilic diblock polyelectrolytes will be examined.[37]

The knowledge of structure–properties relationship in this context represents an exciting and still open scientific challenge and from an applicative perspective can help in designing polymers with the desired rheological characteristics for specific applications.

ASSOCIATED CONTENT

Supporting Information

Details on synthesis and characterization of the polymers; ^{1}H NMR spectra of PS2BMA and PS2MA. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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